Clays and Clay Minerals, Vol. 31, No. 1, 57–59, 1983.

NOTES

HARMOTOME IN A BASALTIC, VOLCANICLASTIC SANDSTONE FROM A LACUSTRINE DEPOSIT NEAR KIRKLAND JUNCTION, YAVAPAI COUNTY, ARIZONA

Key Words—Barium, Harmotome, Lacustrine, Volcaniclastic, Zeolite.

Harmotome, probably the most common of the barium-rich zeolites, has been reported from a variety of metamorphic and igneous rocks throughout the world (Deer *et al.*, 1963). Harmotome, however, seems to be a rare authigenic constituent in sedimentary rocks, and its most common occurrence apparently is in deep-sea sediments where its abundance is minor compared with that of phillipsite and clinoptilolite (Kastner and Stonecipher, 1978). The only previous reports of harmotome from lacustrine rocks are in oil shale of the Eocene Green River Formation in the Piceance Creek basin of Colorado and in silicic tuffs of the Pliocene Big Sandy Formation near Wikieup, Arizona (Sheppard and Gude, 1971).

MATERIALS AND METHODS

The harmotome described herein was discovered in 1981 during an investigation of the zeolites in upper Cenozoic tuffaceous rocks of southwestern Yavapai County, Arizona. The harmotome-bearing sandstone is exposed in a small roadcut on the west side of the U.S. Route 89, about 6 km southwest of Kirkland Junction in the NE¼ SW¼ sec. 5, T11N, R4W. This yellowish-brown, resistant sandstone is about 40 cm thick, and is part of an unnamed lacustrine deposit of Pliocene age (Wilson *et al.*, 1969). The rocks exposed in the roadcut are chiefly brown mudstone, and the harmotome-bearing sandstone occurs in the upper part of the exposed section, about 3 m beneath a basalt flow (Figure 1). Several silicic tuffs rich in clinoptilolite, erionite, or a mixture of clinoptilolite and erionite crop out stratigraphically lower than the harmotome-bearing sandstone.

Specimens of the harmotome-bearing sandstone were studied using the petrographic microscope, X-ray powder diffraction (XRD), and scanning electron microscopy (SEM). Optical and XRD techniques were necessary to characterize the mineralogy of the bulk rock, and XRD analysis of the <2-μm fraction was used to identify the abundant authigenic clay mineral. Optical and SEM techniques were useful to determine the paragenetic relationships of the authigenic minerals, and an energy dispersive X-ray (EDX) attachment to the electron microscope was used to obtain qualitative chemistry of the harmotome.

RESULTS AND DISCUSSION

The harmotome occurs chiefly as a cement in a porous, medium- to fine-grained sandstone that consists mainly of angular to subangular clasts of basalt and minor epiclastic grains of quartz, plagioclase, epidote, and biotite. Thin lenses of granule-size or coarse-sand-size detritus are common in the lower part of the sandstone. Although the individual harmotome crystals cannot be resolved without a microscope, the harmotome cement can be recognized under a hand lens by its appearance as a light-gray film that coats the detrital grains.

The basaltic detritus has a porphyritic and hyalopilitic texture. Phenocrysts of zoned plagioclase (An_{65-55}) and laths of plagioclase (An_{55}) are set in a groundmass that originally was glass but now consists of smectite and noncrystalline iron oxide. Glass originally made up about 30–50% of the basalt. Vague pseudomorphs of an unidentified phyllosilicate mineral represent primary mafic minerals in the basalt.

Smectite is the most abundant constituent in the sandstone, and it occurs as a diagenetic alteration of the basaltic glass.

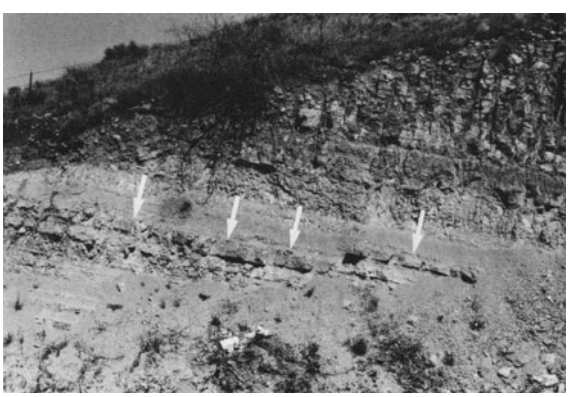

Figure 1. Roadcut on the west side of U.S. Route 89, about 6 km southwest of Kirkland Junction, Arizona, showing basalt flow overlying lacustrine rocks. The harmotome-bearing sandstone (arrows) is cut by a small normal fault.

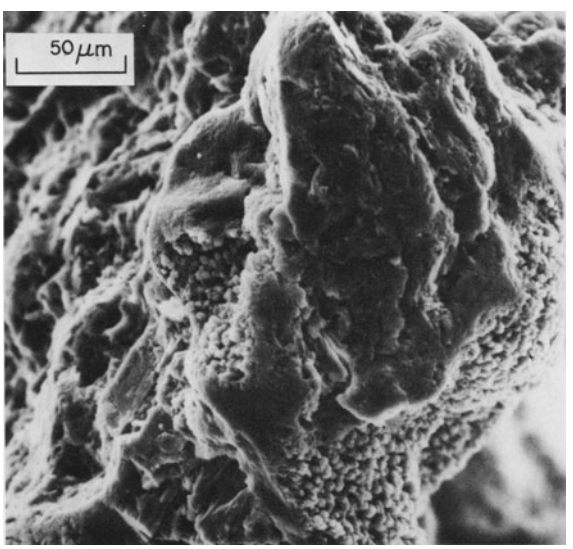

Figure 2. Scanning electron micrograph showing harmotome cement on subangular grains of basalt.

Table 1. X-ray powder diffraction data for harmotome, near Kirkland Junction, Arizona.[1]

hkl	d(calc) (Å)	d(obs) (Å)	I/Io
100	8.09	8.08	75
001	7.11	7.14	100
011	6.36	6.38	46
120	5.33	5.31	10
021	5.02	5.02	37
$\bar{2}01$	4.929		
$\bar{1}02$	4.280	4.282	61
101	4.268		
$\bar{1}31$	4.078	4.073	73
$\bar{2}12$	3.901		
210	3.889	3.887	27
121	3.655	[2]	
012	3.450	[2]	
140	3.241	[2]	
$\bar{3}01$	3.200	3.203	86
041	3.167		
131	3.614	[3]	
$\bar{3}12$	3.125	3.130	40
$\bar{3}11$	3.121	[2]	
$\bar{2}32$	3.076	3.077	25
230	3.071		
$\bar{3}22$	2.919		
$\bar{3}21$	2.915	2.919	39
032	2.840		
$\bar{1}03$	2.738	[2]	
102	2.732	[3]	
$\bar{1}42$	2.727		
112	2.682	2.681	52
$\bar{1}51$	2.672		
221	2.667		
051	2.630		
$\bar{3}23$	2.527	2.526	78
320	2.520		

[1] Diffractometer, CuKα_1 radiation, fluorite internal standard.

[2] Reflection obscured by the reflection of plagioclase impurity.

[3] Reflection obscured by the reflection of the internal standard.

The chemical components of the smectite must have been mobile because a thin film of smectite also coats nonvolcanic grains such as strained quartz and epidote. XRD analysis of the randomly oriented, air-dried, <2-μm fraction of the sandstone showed that d(060) for the smectite is 1.504 Å, indicating that the smectite is dioctahedral and that it is probably montmorillonite (H. C. Starkey, U.S. Geological Survey, Denver, Colorado, oral communication, 1982).

Harmotome makes up about 4–5% of the rock, and it lines voids in the sandstone as a single layer of stubby, prismatic crystals that grew perpendicular to the detrital grains (Figures 2 and 3). Most of the harmotone crystals are 2–7 μm long. Locally, a thin layer (3–5 μm thick) of opal separates the smectite-rich detritus from the harmotome. Complete optical parameters for the harmotome could not be determined because of the small size of the crystals, but the mean index of refraction is 1.506.

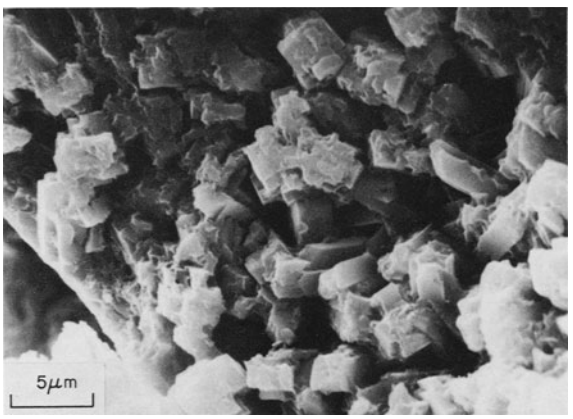

Figure 3. Scanning electron micrograph showing stubby, prismatic harmotome that grew on altered fragment of basalt.

XRD data for the harmotome near Kirkland Junction (Table 1) were obtained from an upgraded, but still impure, fraction of the harmotome-bearing sandstone. The d values for this harmotome compare favorably with those of a diagenetic harmotome near Wikieup, Arizona (Sheppard and Gude, 1971). Cell parameters were obtained by a least-squares refinement of the XRD data, and the resulting monoclinic cell dimensions and volume are $a = 9.859 \pm .009$ Å, $b = 14.15 \pm .01$ Å, $c = 8.670 \pm .008$ Å, $\beta = 124°51' \pm 4'$, and $V = 992 \pm 1$ Å^3.

A chemical analysis of the harmotome-bearing sandstone is given in Table 2. Except for the low MgO and CaO values and the high BaO value, the analysis is consistent with a rock containing mainly basaltic detritus. If all of the BaO is assumed to be in the harmotome, the rock contains about 6% of this zeolite, a value close to the 4–5% estimated by optical examination. The high H_2O content reflects the complete alteration of glass to hydrous minerals, chiefly smectite. Analysis of the harmotome using the EDX attachment to the scanning electron microscope demonstrated that the zeolite has a major barium content and only a minor calcium content. Neither sodium, potassium, nor magnesium was detected. Quantitative

Table 2. Chemical composition of harmotome-bearing sandstone near Kirkland Junction, Arizona.[1]

SiO_2	52.0
Al_2O_3	17.1
Fe_2O_3	8.05
MgO	3.36
CaO	4.77
BaO[2]	1.27
Na_2O	2.42
K_2O	1.01
TiO_2	0.97
P_2O_5	0.26
MnO	0.09
H_2O[3]	8.06
Total	99.36

[1] Field No. KJZ-1-6, laboratory No. D-242749. X-ray spectrographic analysis by J. S. Wahlberg, A. Bartel, J. Taggart, and J. Baker.

[2] BaO determined as barium by inductively coupled plasma/optical emission spectrographic analysis by M. Malcolm.

[3] Loss on ignition at 900°C.

https://doi.org/10.1346/CCMN.1983.0310109 Published online by Cambridge University Press

analysis of the harmotome using the electron microprobe was considered unreliable because of the very small crystal size and the high water content of the zeolite. Thus, this harmotome from Kirkland Junction probably has a composition close to ideal harmotome ($Ba_2Al_4Si_{12}O_{32}\cdot 12H_2O$), and it differs significantly from the alkali-rich harmotome near Wikieup, Arizona (Sheppard and Gude, 1971), the only other lacustrine harmotome for which there is a published analysis.

The above data suggest that the glass of the basaltic detritus reacted with the interstitial lacustrine water during diagenesis to form smectite, harmotome, and minor opal. The smectite crystallized early to form pseudomorphs of the glass and thin coatings on nonvolcanic detritus. Harmotome crystallized late and precipitated on the altered basaltic detritus and on smectite-coated, nonvolcanic grains. The paragenetic sequence of glass → smectite → zeolite is similar to that commonly observed for the diagenetic alteration of silicic, vitric tuffs in lacustrine deposits (Sheppard and Gude, 1973). Although some barium for the harmotome may have been derived from the basaltic glass, most probably was supplied by the interstitial water. The barium apparently remained in the fluid phase during early diagenesis, became concentrated, and then was incorporated in harmotome, the last phase to crystallize.

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(Received 25 August 1982; accepted 18 October 1982)